NATURE OF THE FREE RADICALS IN COALS, PYROLYZED COALS, AND LIQUEFACTION PRODUCTS

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Electron spin resonance (ESR) spectrometry has been the favored instrumental tool to probe the nature of the free radicals in coals and materials derived from coal (1). Recently, it was shown that these free radicals are also amenable to study by electron nuclear double resonance (ENDOR) spectrometry (2,3). The ENDOR technique is becoming increasingly popular in free radical studies because frequently the resulting spectra are much more highly resolved than corresponding ESR spectra of the same materials (4).

As a first step toward elucidating the role of free radicals in the liquefaction of coal, the stable radicals present in coals, pyrolyzed coals, and liquefaction products require characterization. In the present characterization study we have applied both the ESR and ENDOR techniques. For many of the samples examined, it was found that great care must be taken during sample preparation to ensure reliability of the spectral data.

Coals. ESR measurements on non-anthracitic and young anthracitic coals can be made with little difficulty. It is best to evacuate the samples since it has been shown that the ESR spectra of fusains, petrographic constituents found in nearly all coals, are quite sensitive to the presence or absence of air (oxygen) in the sample (5). Contrary to other evidence in this report (5), high rank anthracites and meta-anthracites do require dilution of the samples with a non-conducting medium to prevent errors in ESR measurements due to microwave skin effects. For example, the ESR intensity of a meta-anthracite from Iron County, Michigan increased significantly rather than decreased after the sample was diluted with KBr.

For non-anthracitic coals, the observed variation of the ESR g value with coal rank suggested that the naturally occurring radicals in coals become more "hydrocarbon-like" as coalification progresses (6). Evidence supporting this hypothesis is depicted in Figure 1. The plot of ESR g values vs oxygen contents of the coals suggests that the unpaired electrons in low rank coals interact with oxygen atoms in the sample. Statistical treatment of the data revealed that the g values of only two of the coals fall outside the area bounded by the dashed lines drawn $\pm$ twice the standard error of estimate from the linear regression line. These two coals are somewhat unique in that they contain an usually high content of organic sulfur (7). In the second plot of Figure 1, the abscissa has been changed to reflect the sum of the oxygen and sulfur contents of the coals, (each element being weighted according to its spin-orbit coupling constant). This latter plot exhibits much better statistics, suggesting that the unpaired electrons interact with sulfur as well as with oxygen. Attempts to extend the statistical treatment to nitrogen in the samples were inconclusive.

Pyrolyzed Coals. A number of investigators have applied ESR techniques to pyrolyzed coals (1). At least two groups of investigators (8,9) have reported g values less than that of the free electron for certain coals heated to commonly used liquefaction temperatures. One group (9) attributed these low g values to the

presence of sigma radicals. During the present investigation, we observed a similar g value dependence with heat-treatment temperature for hvAb coal from the Ireland Mine (Pittsburgh bed) in West Virginia.

It had been shown previously (10) that incorrect ESR g values were obtained for heat-treated sucrose if proper dispersal techniques were not used. With this in mind, we measured the effect of sample dilution on the apparent g value of Ireland Mine coal heat-treated to 450°C. The results, shown in Figure 2, show that the true g value of the sample in question is actually higher than that of the free electron. This suggests that great care must be exercised when applying ESR techniques to heat-treated coals. This problem will undoubtedly present some obstacles to the in situ ESR studies of coal pyrolysis and coal liquefaction planned by many laboratories.

Liquefaction Products. A few ESR studies of liquefaction products from coal have been reported (6,11,12). One group of investigators (6) concluded from ESR studies of coal-derived asphaltenes that charge-transfer interactions are relatively unimportant binding forces between the acid/neutral and base components.

ESR results from our on-going efforts to elucidate the changes in chemical structure that occur during coal liquefaction are given in Table 1. The samples examined were obtained from a liquefaction run in the Pittsburgh Energy Technology Center's 10 lb coal/hr process development unit (13). The run was made without added catalyst. The samples included the process coal and its pyridine extract, and the preasphaltenes, asphaltenes, and oils separated from the centrifuged liquid product. It can be seen that the free radical contents change in the order: process coal < preasphaltenes >> asphaltenes > oils. The g values suggest the presence of "hydrocarbon-like" radicals with perhaps some interaction between the unpaired electrons and heteroatoms in the asphaltene and oil fractions. The line widths appear to increase (at least crudely) with increasing hydrogen contents of the samples.

ENDOR Studies. In contrast to the ESR spectra of coals, which generally consist of a single line devoid of any resolvable fine structure due to hyperfine interactions, the ENDOR spectra (at least in the present study) are rich in detail (Figure 3). These results are quite surprising in light of spectra published several months ago which showed only a single band at the so-called free proton frequency (2). In an attempt to experimentally deduce the reasons for this apparent discrepancy of results, we found a reversible effect of air (oxygen) on the ENDOR spectrum, i.e., the hyperfine lines were observed for evacuated samples, but disappeared upon admission of air to the samples.

The fact that an ENDOR spectrum is observed under the experimental conditions employed is unambiguous proof that the unpaired electrons in the coal couple with nuclear spins, undoubtedly protons, in the sample. This provides additional support for the free radical interpretation of the ESR spectrum. The magnitude of the hyperfine interactions, i.e., none greater than 10 gauss, indicates that none of the radicals has a high unpaired electron spin density at a particular carbon atom.

Table 1. MAF analyses, carbon aromaticities, and electron spin resonance data for materials produced from the liquefaction of West Virginia (Ireland Mine) hvAb coal in the Pittsburgh Energy Technology Center's 10 lb coal/hr process development unit.

	COAL		PREASPHALTENES	ASPHALTENES	OILS
	Solid Coal	Pyridine Extract			
MAF Analysis, %					
C	78.5	81.7	86.9	87.3	86.6
H	5.6	5.9	5.1	6.3	8.2
O	9.7	8.0	4.8	3.6	3.3
N	1.2	1.9	2.2	2.0	1.2
S	4.9	2.6	0.9	0.9	0.7
f_a	0.76[1/]	0.73[1/]	0.84[1/]	0.77[2/]	0.63[2/]
ESR Data					
Free Spins/Gram	1.4×10^{19}	9.0×10^{18}	2.0×10^{19}	2.4×10^{18}	9.4×10^{17}
g value	2.0027_7	2.0031_2	2.0027_9	2.0032_9	2.0030_7
Linewidth, gauss	5.9	5.7	6.6	7.3	8.7

[1/] f_a determined by cross-polarization ^{13}C NMR.

[2/] f_a determined by high-resolution ^{13}C FT NMR.

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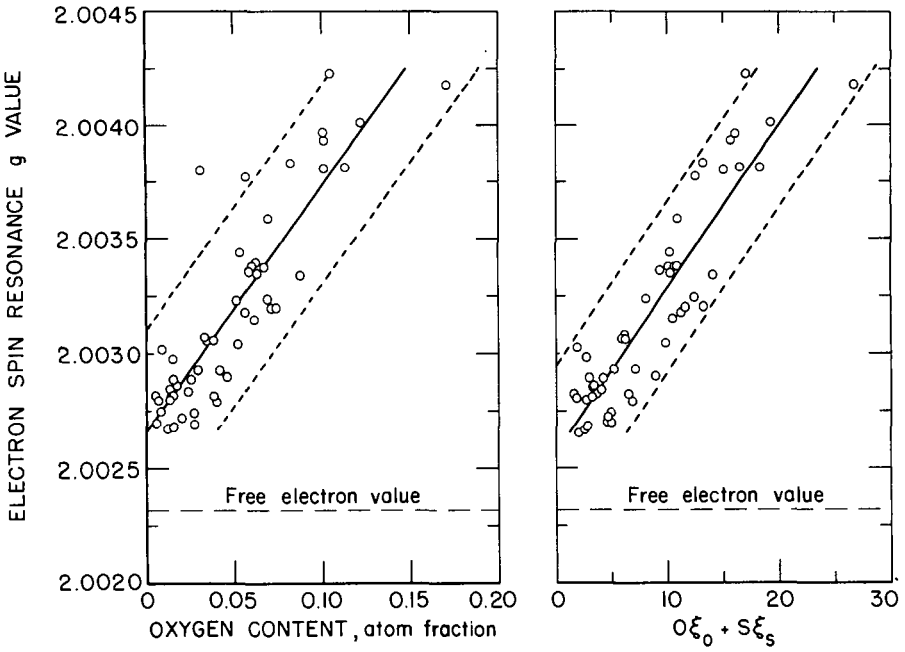

Figure 1. Functional dependences of the electron spin resonance g values of vitrains from selected coals.

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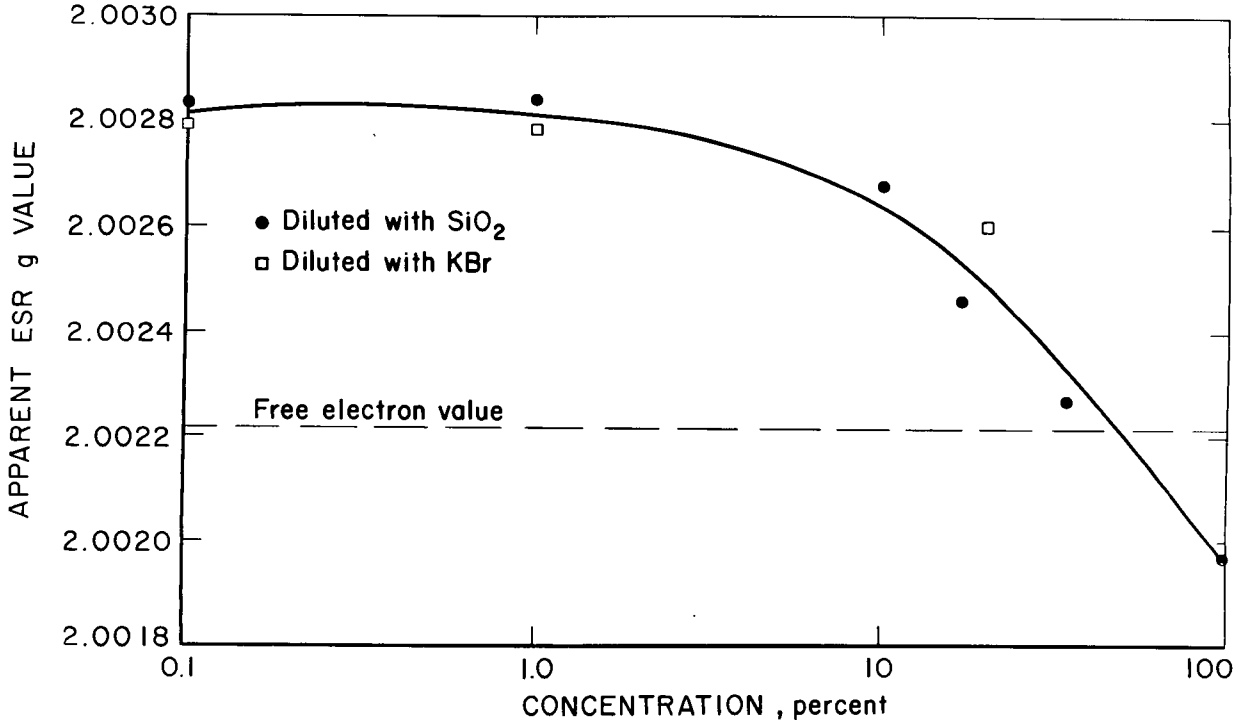

Figure 2. The effect of sample dilution on the apparent electron spin resonance g value of Ireland Mine hvAb coal heat-treated to 450°C.

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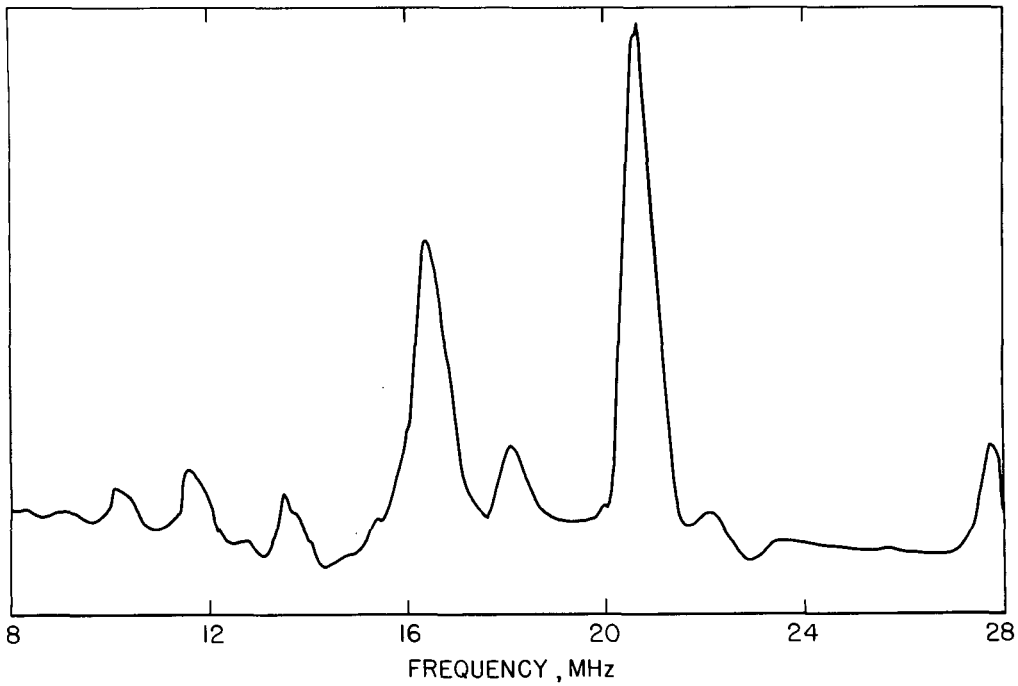

Figure 3. Electron nuclear double resonance (ENDOR) spectrum of vitrain-rich Pittsburgh coal.

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